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Features of the Crystal Structure and Electrical Properties of Sodium Chloride at Pressure 20–50 GPa

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Abstract—The electrical properties of polycrystalline samples of sodium chloride are studied at direct and alternating current in a wide range of frequencies at high pressure and room temperature. Graphic analysis of the experimental data [1–3] in the view of equivalent circuits allowed us to separate the contributions to conductivity caused by grains and intergrain boundaries. Features of impedance at pressure up to 37 GPa are in good agreement with earlier data and structural changes. It is shown that in the studied materials the electrical resistance of grains is much greater than the resistance of intergrain boundaries.

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INTRODUCTION

At ambient conditions, crystals of sodium chloride have fcc structure. The radii of chlorine ions (0.181 nm) and sodium (0.098 nm) differ almost twofold. Under the action of high hydrostatic pressure in sodium chloride, a transition from the structure of NaCl (O_h^5, $Z = 4$) to the structure of CsCl (O_h^1, $Z = 1$) is observed with a rather large jump in volume (~10%). The mechanism for such $B1-B2$ transitions is the compressive strain and the shear strain of atoms located in plane (001) of a face-centered cubic cell in the direction of ±[110] [4].

It is known that this structural phase transition is observed at pressures of ~29 GPa. This transition has been investigated in detail by structural, optical, and electrical methods [5, 6]. As was shown earlier, the structural $B1-B2$ transition is accompanied by a substantial decrease in the electrical resistance of NaCl, and the electric conductivity has a hysteresis. At pressures 29–37 GPa, the conductivity is of an activation nature with energy that varies from 0.015 eV at 29 GPa to 0.003 eV at 37 GPa. At 38 Gpa, the resistance of a sample is reduced by ~30%, and the temperature coefficient of the resistance becomes positive. The carrier concentration, estimated from the values of thermopower, is at least 2–3 orders of magnitude lower than in ordinary metals [7, 8].

At the same time, it is known that the structure of CsCl is stable up to 100 GPa, and no changes in the structure of sodium chloride have ever been observed at pressure ~37 GPa. The aim of this work was therefore to study structure of sodium chloride at pressures above the structural phase transition and establish correlations between structural changes and electrical conductivity.

EXPERIMENTAL

Electrical measurements were carry out in a Vereschagin–Yakovlev's diamond anvil cell (DAC) with anvils of "rounded cone-plane" type. The anvils are made of electrically conducting synthetic carbonado-type diamonds and can be used sa cintacts ti sample. DAC resistance did not exceed 15 Ohm and was not dependent on pressure. Our DAC was calibrated on pressure-induced phase transitions of some compounds (GaP, ZnS), which are standards of pressure. The method of pressure estimation was described in [10, 11]. The diameter and thickness of sample in DAC is about 200 microns and 20 microns accordingly.

Measurements of impedance spectra were performed using a Solartron FRA-72. Amplitude of the sine wave was 10 mV; the frequency scanning range was 1 Hz to 20 kHz.

In situ X-ray diffraction measurements of NaCl were carry out in a classical daimond anvil cell (DAC) on a high-brilliance X-ray system Bruker APEX CCD, using Mo K_α characteristic radiation ($\lambda = 0.7115$ Å). The method was described in detail in [12]. The size of the coherent scattering regions (CSRs) was determined from the broadening of diffraction lines by Selyakov–Sherer method.

RESULTS AND DISCUSSION

Figure 1 shows the impedance spectra of polycrystalline NaCl at different pressures. It can be seen from the figure that the separation of spectra is possible only up to a certain pressure. The hodographs of the impedance are two overlapping semi-circles whose arcs intersect some of the resistance values on the real axis. Solid lines are the results from graphoanalytical calculations. At pressure increasing up to 37 GPa the hodo-

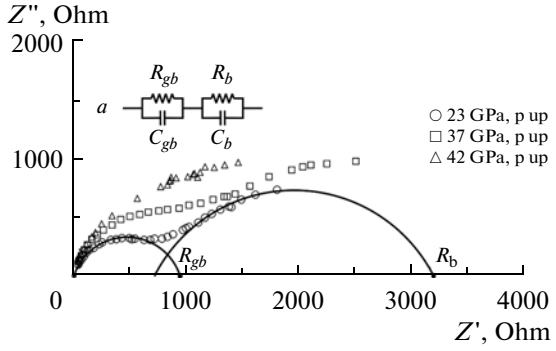

Fig. 1. Impedance hodographs modifications of DAC with NaCl sample at different pressures. Insert: Equivalent electric circuit in which *Rg* and *Cg* are the resistance and capacity of grains, and *Rgb* and *Cgb* are the resistance and capacity of the intergrain boundary.

graphs of impedance were approximated by two slightly overlapping semi-circles with centers that grew closer as the pressure increased and the overlapping of the semi-circles becomes more pronounced. At pressure about 42 GPa, the impedance hodograph became a single semi-circle.

The equivalent circuit used to approximate the impedance hodographs shown in insert *a* of Fig. 1 consisted of two series-connected parallel *RC* chains: (*Rgb*, *Cgb*), which characterizes the resistance and capacitance of intergrain boundaries, and (*Rg*, *Cg*) characterizing the resistance and capacitance of grains of polycrystalline NaCl [12, 13]. The numerical values of the resistance of *Rg* and *Rgb* were obtained from the points of intersection between semicircles and the axis of real resistance *Z'*, while the capacitance values were obtained from the maximum value of the imaginary (capacitive) part of the impedance according to the formula for calculating the relaxation time of an *RC* circuit: $\tau = RC = \frac{1}{\omega} = \frac{1}{2\pi f_{\max}}$, $2\pi f_{\max} RC = 1$.

The baric dependences for the resistance of grains and intercrystalline boundaries are shown in Fig. 2. The resistance of the grains and intergrain boundaries grew with increasing pressure (Fig. 2a and 2b), and change slightly at pressures above 37 GPa. The increased resistance of grains upon a rise in pressure could be due to baric recrystallization of the grain (the growth of grains containing a great deal of defects), while the increased resistance of the intergrain boundary could correspond to a reduction in defects, thickness, and the angle of rotation [15, 16]. An increase in pressure lowers the capacity of the grain and intergrain boundaries, and the capacities are virtually unchanged at pressures above 37 GPa. It was found earlier that at pressures near 37 GPa in NaCl, the character of the temperature dependence for the resistance changes, while the pressure dependence of thermoelectromotive force has a maximum (Fig. 3) that is probably due to the formation of the sample's internal structure, particularly pressure-induced reversible amorphization or the dispersion of the sample due to the inhomogeneity of the applied pressure.

Figure 4 shows the volume (parameter) dependence of the crystal lattice of sodium chloride on pressure. The dependence $a(p)$ can be approximated by

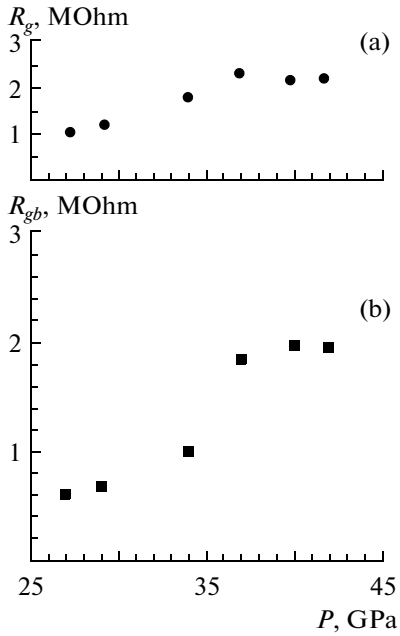

Fig. 2 Baric dependences of the resistances of *Rg* grains (dots) and intergrain boundaries *Rgb* (squares).

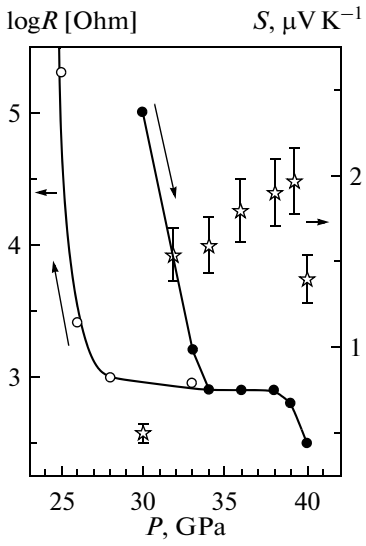

Fig. 3. Pressure dependences of resistance (black dots represent the pressure loading; white dots, the pressure unloading) and thermoelectromotive force (stars) of sodium chloride on pressure.

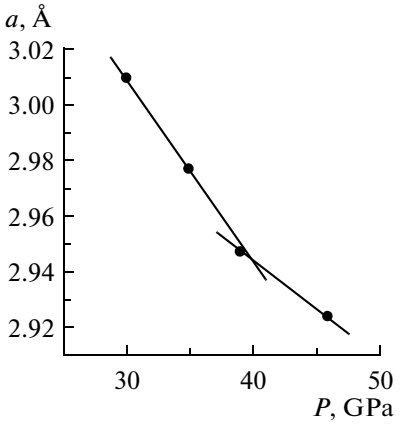

Fig. 4. Baric dependence of the crystal lattice parameter of NaCl.

straight lines in two pressure regions. A more rapid drop in lattice parameter *a* is observed in the pressure range up to 37 GPa, and parameter decreases more slowly in the range of 37–45 GPa.

The size of the coherent scattering regions (CSR) increases as the pressure rises. The size of a CSR is determined from the data on the broadening of diffraction reflections; it is used to estimate the size of the crystallites in polycrystals and is identified from the average crystallite size. The CSR size is typically 10–15% lower than the results from determining the grain size, since the coherent scattering region corresponds to the internal (ordered) grain region and does not include strongly distorted borders [14, 15]. Thus the grain size of polycrystalline NaCl (and the CSR size) is greatest at a pressure of 37 GPa.

A change in the nature of the impedance hodographs and the growth of the interphase boundaries in the NaCl sample were observed in the same pressure range.

CONCLUSIONS

The effect of high pressures on the baric dependences of electrical characteristics (resistance and capacitance) of the grains and intergrain boundaries of samples of NaCl was analyzed. It was shown that the contribution from the intergrain border to the conductivity of alkali metal halides dominates. At pressures above 42 GPa, the contributions to the resistance of a sample on its grains and boundaries are indistinguishable.

From the baric dependences of the capacitance of grain boundaries, we can indirectly study their development dynamics. At pressures up to 37 GPa, the reduced capacity of grain boundaries could indicate an increase in their area (i.e., the maximum dispersion of the system at this pressure).

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